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ORIGINAL ARTICLE

The Effect of Oxidation on the Tribological Performance of Few Vegetable Oils

Jagadeesh K. Mannekote[1], Satish V. Kailas[1,*]

[1]*Department of Mechanical Engineering, Indian Institute of Science, Bangalore, India.*

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Background: The use of vegetable oils and their derivatives as lubricant base oils are ever increasing because of sustainability issues and in the context of conservation of nature as they are biodegradable and environmentally friendly. The one disadvantage which is of concern with vegetable oils is their limited oxidative stability. Objectives: To study the effect of oxidation on the tribological performance of few vegetable oils by subjecting the oil samples to accelerated ageing in a dark oven at different temperatures, inducing the oxidation under controlled conditions. Method: Oils were stored at an elevated temperature in an oven under dark condition and the oxidized oil samples were analyzed in terms of various properties. Results and conclusions: The samples were analyzed for the changes in viscosity, percentage of free fatty acid, peroxide number and were compared with fresh oils samples. Further tribological property was also evaluated and the observed differences were linked to formation of oxidation products like peroxides, kinetics of the oxidation with reference to ageing temperature.

KEY WORDS: Vegetable oils; Fatty acids; Oxidation; Four ball test.

1. Introduction

Lubricants and greases based on vegetable oils are in use since ancient times, as the use of natural products to achieve lubrication effect dates to antiquity[1]. Most lubricants available today are mineral oil based compounds, which have become prominent ever since the discovery of petroleum as they have superior quality at an affordable price[2]. At the same time they are "non-renewable" and cause damage to the environment. Since the biodegradability and toxicity are the most important concerns, use of environmentally friendly products are gaining popularity to replace the mineral oil based products in sensitive applications[3]. The use of renewable source not only enables efficient carbon cycling but also reduces CO_2 emissions[4]. The use of vegetable oils for lubricant applications is very significant in terms of protecting the environment[5].

Typically most of the vegetable oils are very similar in structure with varied amounts of fatty acids having different carbon chain lengths and saturation levels besides other functional groups may also present in certain oils like castor[6]. Chemically, these are esters of glycerin with long-chain fatty acids, where the fatty acid components are variable as they are plant-specific. Fig. 1 shows the schematic representation of vegetable oil in which three different acid moieties are attached to the glycerin molecule through the ester linkage. This similarity in their structure makes most of the vegetable oils exist in only a narrow range of viscosities limiting their applications as lubricants.

*Corresponding author.
E-mail address: satvk@mecheng.iisc.ernet.in (S.V. Kailas)

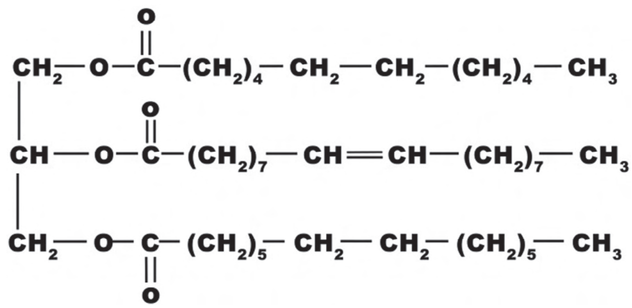

Fig. 1 Schematic representation of triglyceride structure.

The triglyceride structure of vegetable oils strongly interacts with metallic surfaces resulting in reduced friction and wear, forming a high strength lubricant film. These strong intermolecular interactions are also resilient to changes in temperature resulting in high viscosity coefficient though most of the oils have very narrow range of viscosity. Since the primary difference among the various vegetable oils is in the amount of saturated or unsaturated fatty acids and in the degree of unsaturation in the molecule, it reflects in the variations observed with reference to the tested oil samples.

Vegetable oils are sensitive to temperature and will undergo oxidation rapidly. This also results in releasing the fatty acids from the triglyceride structure by hydrolysis reaction which is primarily catalyzed by the oxidation process. The oxidation process results in deteriorating the quality of the oil which in turn will have great influence on the product quality and shelf life of the vegetable oil based lubricants. Thus, understanding oil oxidation process will be very essential while formulating biodegradable lubricants[7]. Since lipid oxidation is a slow process at room temperature, employing an accelerated method will be very useful to estimate the oxidative stability or the induction period in a relatively short period of time. Different methods are used to increase the rate of the reaction such as the temperature, use of metal catalysts, and increasing the oxygen partial pressure in a closed container, of these the first one is usually chosen to accelerate the oxidation process as the rate of the reaction increases exponentially with the absolute temperature[8].

2. Materials and Methods

The present study focuses on the effect of oxidation on Groundnut, Palm, Rice bran, Soybean and Sesame oils. The commercial grade samples were used without further purification for all experiments. The composition of the Groundnut, Palm, Rice bran, Soybean, and Sesame oils were analyzed by means of Gas Chromatography (GC). The vegetable oils were converted into their corresponding Fatty Acid Methyl Easter (FAME) by mixing 1 mL of hexane, 0.1 mL of vegetable oil, 1 mL of sodium methoxide and the resulting mixture was stirred vigorously. The FAMEs layer from the mixture was collected for GC analysis. The fatty acid composition of different vegetable oils was determined by identifying the peaks in terms of retention times in GC[9]. The composition of the test oils in terms of constituent fatty acids is shown in the following Table 1.

In the present work Groundnut, Palm, Rice bran, Soybean and Sesame oils were stored at an elevated temperature in an oven under dark conditions to avoid the influence of photo-oxidation. The oxidized oil samples were collected periodically and further analyzed in terms of various physical and chemical tests. In addition, the tribological properties of these samples were also evaluated by using a standard four ball tester machine. The results of these tests were used to judge the influence of chemical changes on the tribological properties of selected base oils.

2.1 Accelerated Ageing of Vegetable Oils

Accelerated ageing of vegetable oil samples was simulated by storing the groundnut, palm, rice bran, soybean, and sesame oil samples in a dark oven at 60°C and was based on the version of American Oil Chemists Society (AOCS) rec-

Table 1 Fatty acid composition of vegetable oils

#Fatty Acid name	Wear Step				
	Groundnut oil	Soybean oil	Rice bran oil	Sesame oil	Palm oil
Capric Acid (C 10:0)	0.2	–	0.2	–	–
Lauric Acid (C 12:0)	1.6	–	0.2	0.4	0.4
Myristic Acid (C 14:0)	1.3	0.3	0.7	0.2	1.0
Palmitic Acid (C 16:0)	12.3	10.8	29.6	10.7	41.1
Palmitoleic Acid (C 16:1)	–	0.3	2.5	0.2	1.6
Stearic Acid (C 18:0)	4.1	3.2	4.1	5.2	4.9
Oleic Acid (C 18:1)	47.8	22.4	47.5	41.4	43.1
Linoleic Acid (C 18:2)	28.6	54.0	13.1	40.4	7.9
Linolenic Acid (C 18:3)	–	6.8	1.2	0.5	–
Arachidic Acid (C 20:0)	1.2	0.2	0.9	0.6	–
Behenic Acid (C 22:0)	2.9	–	–	0.4	–

#(C X:Y) is a notation where X indicates number of carbon atoms and Y indicates number of double bonds for a given fatty acid chain.

ommended practice[10]. Dark oven conditions were used to eliminate the possibilities of photo-oxidation. About 900 mL of groundnut, palm, rice bran, soybean, and sesame oil samples were taken in one liter beakers and stored in an oven at the specified temperature, the oil samples were removed at an regular intervals of 14, 28, 42 days for further analysis and were compared with a fresh oil sample which was used as reference in the present study. Further the ageing process was also carried out at 80°C and 100°C in order to see the influence of temperature on the process.

2.2 Kinematic Viscosity of Vegetable Oils

Kinematic viscosity, an important physical property of base oils, is a measure of oil's flow characteristics. Although the significance of viscosity is important from the standpoint of new oils, it also has relevance in the evaluation of base oils, as well as used lubricating oils. In the present work, kinematic viscosity of fresh and aged oil samples collected from the oven at regular intervals was determined according to the ASTM Standard D445-09 using previously calibrated U-tube viscometers in a constant temperature bath capable of maintaining the temperature with an accuracy of ± 0.1°C[11].

2.3 Free Fatty Acid and Peroxide Value of Oil Samples

The percent of free fatty acid of fresh and aged oil samples collected at regular intervals of 14, 28 and 42 days was evaluated using the AOCS official method based on the titration of sample against standardized NaOH solution. In addition to that, the peroxide values of the aged oil samples were also determined by using the AOCS method[12,13].

2.4 Tribological Evaluation of Test Oils

In the present work tribological performance of the fresh and aged groundnut, palm, rice bran, soybean, and sesame oil samples were carried out using a four-ball tester at 1,200 rpm, 400 N, 75°C, and 60 min. Chrome alloy steel balls, confirming to AISI standard steel nº E-52100, with a diameter of 12.7 mm, Grade 25 EP (extra polish), having Rockwell C hardness of 62 were used for the tests[14]. The test balls were thoroughly cleaned with hexane, before each experiment. The ball pot with cleaned balls and test sample was assembled and tests were conducted. The schematic representation of ball pot with chuck is shown in Fig. 2. Once the experiment was over, the test balls were cleaned with hexane and the wear scar images were captured with digital camera. The diameter of the wear scar was measured using the software with an accuracy of ± 2 µm.

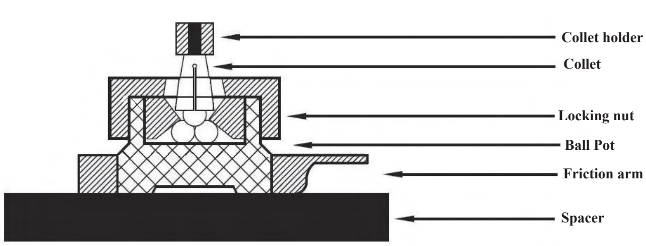

Fig. 2 Schematic representation of the ball pot and chuck in a four ball tester.

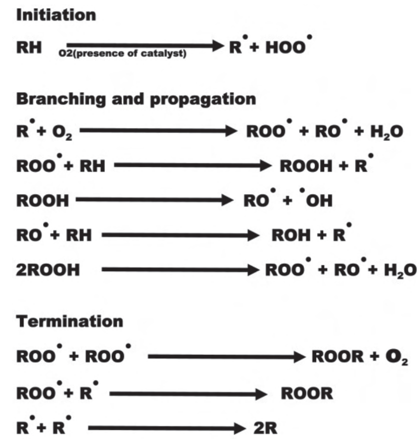

Fig. 3 Schematic representation of oxidation reactions.

3. Results and Discussion

Different assumptions have been put forward to explain the oxidation mechanism ever since the lipids have become subject of interest. The auto-oxidation of the vegetable oils, olefins, is produced by a chain reaction where the oxygen molecule is added to a carbon atom adjacent to a double bond to form a hydroperoxide having a double intact link. The auto-oxidation mechanism essentially a free radical chain reaction consists of the following distinct reaction steps: initiation, propagation, branching and termination. A classical representation of these reactions is shown in Fig. 3.

Majority of vegetable oils are susceptible to oxidation as they contain unsaturated fatty acids, greater the amount of unsaturation more susceptible the oil becomes to oxidation. The process is initiated by the formation of free radicals which react with oxygen to form a peroxy radical as an intermediate product. This peroxy radical then attacks another lipid molecule to form a hydroperoxide and another free radical, thus propagating the oxidation process. Hydroperoxides continue to build-up in the oil, which decompose into secondary compounds like epoxides and polymeric compounds[15].

Kinematic viscosity of fresh and aged oil samples were carried out at 40°C, according to the standard. From Fig. 4, it can be seen that all the oil samples have shown an increase in viscosity with ageing temperature. Further it was noted that the observed change in viscosity was greater when the samples were aged at a higher temperature for a given duration. The increase in viscosity with ageing is basically due to the oxidation and subsequent formation of polymeric compounds resulting from the reaction between the oxidation products formed during the ageing[16].

It was observed that the accelerated ageing of the vegetable oils has resulted in formation of free fatty acid. The corresponding variation of free fatty acids with ageing for different vegetable oil samples subjected to accelerated ageing process is shown in Fig. 5. This is generally initiated with formation of free radical compounds resulting in forming peroxides and hydroperoxides as major products, which consequently play a major role in the formation of free fatty

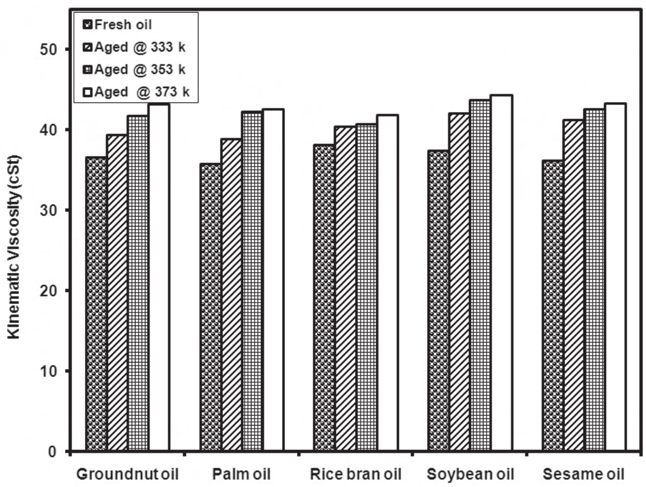

Fig. 4 Variation of kinematic viscosity with ageing temperature for oil samples.

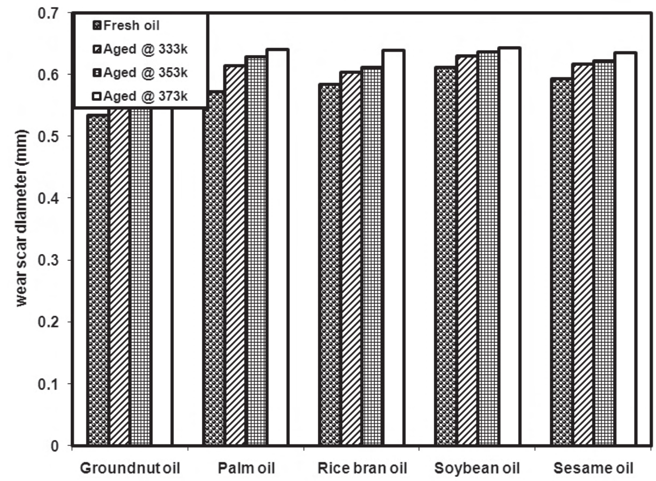

Fig. 6 Variation of wear scar diameter with ageing temperature for oil samples.

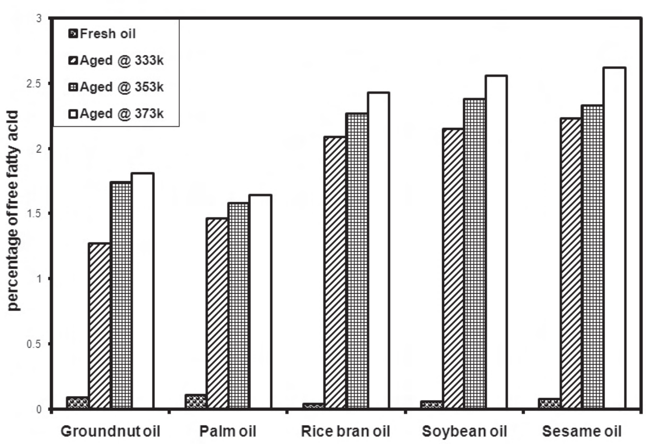

Fig. 5 Variation of percentage of free fatty acids with ageing temperature for oil samples.

acids during the degradation process. It was noticed that the increased amount of free fatty acid was formed with aging temperature for all the oil samples indicating that temperature has an effect on the oxidation. It was also observed that the relative amount of free fatty acid formed was greater for the oils having the higher percentage of unsaturated fatty acids in their composition. Taking these factors into account, by measuring free fatty acid content one can possibly quantify the extent of degradation under specified conditions.

The chemical structure of lubricant plays an important role in the adsorption process as it determines the relative polar attraction of the molecules for the active sites on the surface and how they interact with the surface materials. The effective boundary lubrication with vegetable oils arises from the formation of properly oriented adsorbed surface films on the solid surface of polar molecules to form a close-packed monolayer strengthen the adsorbed film with lateral cohesive forces resisting the penetration by asperities. The variation of wear scar diameter with ageing temperature for oil samples tested in the present investigation is shown in Fig. 6. The relative difference in wear scar diameter is related to extent of protection layer formed by the samples[17].

The variation of the peroxide number with temperature for different oil samples is shown in the Fig. 7. It clearly shows that initially the peroxide level was very small but with ageing an increase in the content of peroxide level was observed. This quantitative difference in the properties of the oils is explained in terms of their composition. Vegetable oils having more saturated fatty esters have shown relatively better oxidation stability compared to the oils with significant amounts of polyunsaturated fatty acids, which are highly susceptible to oxidation, leading to the formation of oxidation products. These products are unstable and as their level builds-up a part of them decompose forming various secondary products[18]. There is a continuous reaction between these peroxides and its derivatives with the surface causing increased wear with ageing duration and temperature.

In addition to that as observed in the previous section with aging the formation of free fatty acids also increases which is results in the degradation of the triglyceride structure. The presence of moisture which exists in the system results in the formation of iron soaps of fatty acids under

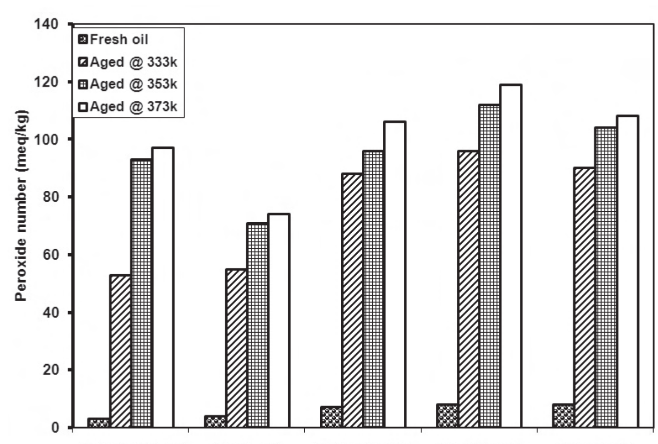

Fig. 7 Variation of peroxide level with ageing temperature for oil samples.

sliding conditions. These metallic soaps are having low-shear strength offering low resistance to shear, and hence, account for the observed low coefficient of friction with ageing duration and temperature, as with ageing, free fatty acid build-up will increase, facilitating the formation of metallic soaps, resulting in a decrease of coefficient of friction as shown in the Fig. 8[19].

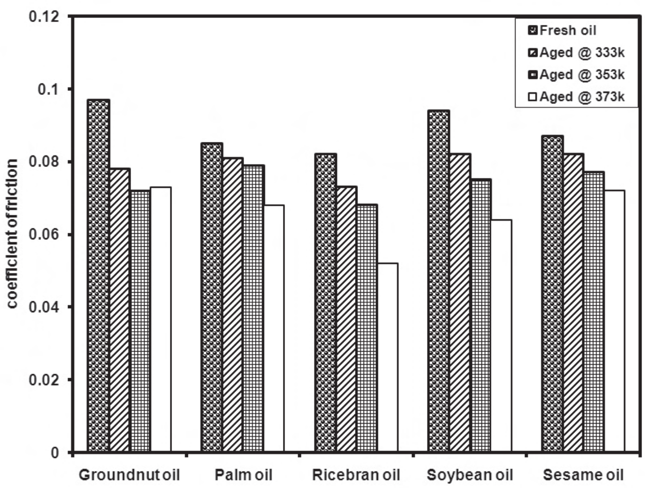

Fig. 8 Variation of coefficient of friction with ageing temperature for oil samples.

4. Conclusions

This study was focused on the boundary lubrication properties of few vegetable oils subjected to accelerated ageing under controlled conditions. The tribological studies were carried out with the aid of four ball tester. Other variables were ignored to focus on the effects of ageing temperature on oxidation and its impact on oiliness as observed in a friction testing instrument.

- The ageing temperature has effect on the oxidation of oil samples as the increased free fatty acids, peroxides were observed for all the oil samples;
- the relative difference in fatty acid content, peroxide level and viscosity was due to the varied amount of unsaturated fatty acids present in the oils tested;
- the increased wear observed with ageing time and temperature for all the oils was due to the formation of peroxides;
- the observed low coefficient of friction with four ball test for oxidized oil samples was due to the formation of soft iron soap having low resistance to shear.

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